

Polyurethane materials for passive isolation bearings

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This work has been directed to both civil structures and nuclear facilities. Polyurethane elastomers (PEs) based on polyether diols and aliphatic and aromatic diisocyanates can be used as passive isolation bearings in building applications. In the present study polyetherdiol, aliphatic or aromatic diisocyanate have been used in polyurethanes, using glycerine, ethylene or diethylene glycols as chain extenders. The effect of varying the concentrations of diisocyanates and structure of chain extenders on PEs has been discussed in respect to mechanical properties. IR and thermal analysis techniques (TGA) were used for material characterization. The results reveal that aliphatic character of diisocyanates lowers the temperature required to achieve the flexibility in the polymer. Based on their mechanical properties, PEs has great potential for applications where wind and earthquake loads resistance, dynamic-to-static stiffness ratio and vertical and lateral load characteristics are required.

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1. Introduction

The protection of nuclear and civil structures from the devastating effects of earthquakes has focused intense research and development throughout the world. Seismic isolation is an effective means for reducing and even eliminating the devastating effects of earthquakes on people, equipment and structures. Seismic isolation equipment is placed between the ground and the structure. The isolators effectively decouple the structure from the strong earthquake motion.

Polymers can absorb mechanical energy and convert this energy partially into heat through viscous deformation [1].

Polyurethane elastomers (PEs) have a unique property of shape memory. These materials (PEs) basically consist of two phases, a frozen phase and a reversible phase [2-6]. Thermally reversible phase maintains a transient shape, while fixed structure allows the recovery of the original shape. Shape memory property is governed by glass transition and melting temperature of polymer segments [7]. Polyurethanes (PUs) are formed by linear polymeric chains of segmented structure.

Most of conventional PUs is based either on polyester or polyether polyols, 4,4-diphenylmethane diisocyanate (MDI) as an isocyanate component and 1,4-butanediol (BDO) as a chain extender [8].

Development of PUs soft grades (having hardness about 70-85 Shore A) has been reported among the latest trends that are taking place in the PU market. The main interest of researchers is focused on the polyol components [9].

Polyurethanes based on polybutadiene polyols could fall into this category. Moreover, they are known for excellent hydrophobicity, hydrolytic and chemical resistance, electrical insulation properties and low-temperature elasticity [10,11].

Various polyurethanes [12,13,14] offers good promise in applications such as sensors, actuators and biomedical purposes.

In this study, shape memory PEs based on polyether diol (PED), 4,4-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI) and glycerine, ethylene or diethylene glycols as chain extenders were synthesized. By introducing the chain extender with different rigidity, it may provide the change in the degree of phase mixing, hard domain structure and hydrogen bonding. The thermo-mechanical properties have been studied to assess the building isolators properties of synthesized polymers.

2. Experimental

2.1 Materials

All chemicals used in this study are listed in Table 1 and they were used as received from the suppliers unless otherwise stated. Polyether diol (PED) and chain extenders were checked for the content of moisture and, if it would be necessary, they were dried under a vacuum until the content of water was below 0.03%.

Table 1. Materials used to obtain polyurethane elastomers for passive isolation bearings

Designation	Mol. Wt.	Melting point °C	Boiling point. °C	Density g/cm ³	Refract. index
Ethylene glycol (EG)	62.07	-13	196-198	1.113	1.4310
diethylene glycol (DEG)	106.12	-10	245	1.118	1.4460
glycerine	92.9		182	1.261	1.4740
4,4'-diphenyl methane diisocyanate (MDI)	250.14	42-44	152-156/ 0.2-0.3mm	—	—
1,6 hexamethylene diisocyanate (HDI)	168.2		255	1.040	1.4520
Poli(1,4-butanediol) Terathane 1400	1400	33-36	>110	0.973	

2.2 Preparation of polyurethanes

All the polymers were synthesized by bulk polymerization.

The synthesis of PUs was performed in a one liter glass reactor at normal pressure, under nitrogen blanket and vigorous agitation. The NCO/OH ratio of all formulations was 1.03-1.05. In the case of the prepolymer procedure, polyether diol was reacted with a diisocyanate at 80 °C for 1 hour to yield a prepolymer that was mixed in the second step with chain extenders at 90 °C for 10 minutes. The resulting material was poured into a mold and left to cure at 100 °C for 20 hours, post-curing of the PUs proceeded at laboratory temperature for 7 days. Under these conditions the addition of catalyst was not necessary.

The polyurethane sheets were used for the determination of mechanical and physical properties and for the thermogravimetric study.

2.3 Measurements

IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellet technique.

Hardness was measured on Instron Shore Durometer using scale-A.

Stress-strain measurements were performed on dumbbell-shaped samples cut from thin films at room temperature on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein Germany. Measurements were run at an extension rate of 10 mm/min, at 25 °C.

Thermogravimetric analyses were performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary) in a temperature range from 0-700 °C. The heating rate was 12 °C/min in air atmosphere and sample size was 50 mg.

3. Results and discussion

The following parameters of the formulation were tested in order to find out the structure-property relationship of the chain extenders based PEs:

- Type of OH groups (primary or secondary) of the chain extenders diol and its molecular weight
- Selection of the diisocyanate
- Hard segment content

The first syntheses were performed using polyether diol and adopting the prepolymer approach.

Table 2. Hardness of the polyurethanes obtained.

Nr.	Designation Samples	Rate Polyeter/Diisocyanate/ Chain extenders	Diisocyanate	Chain extenders	Hardness Shore A
1.	PU1	1:2:1	MDI	EG	75
2.	PU2	1:2:1	MDI	DEG	65
3.	PU3	1:3:2	MDI	EG	85
4.	PU4	1:3:2	MDI	DEG	85
5.	PU5	1:2:1	HDI	EG	55
6.	PU6	1:2:1	HDI	DEG	52
7.	PU7	1:3:2	HDI	EG	55
8.	PU8	1:3:2	HDI	DEG	53

PED, HDI and EG or DEG lead to polyurethanes with Shore hardness about 50, that may be classified as PUs soft grade. PED, MDI and EG or DEG lead to polyurethanes with Shore hardness about 65-85. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

For to obtain softer PUs, a series of samples with decreasing hard phase content was synthesized (Table 2, formulations 1-8). By increasing the hard segment content, it was possible to prepare a PU with hardness as low as 50 Shore

The role of chain extenders molecular weight and of the type of OH groups can also be seen from the Table 2. All these elastomers have similar properties, however, the use of ethylene glycol resulted in an increase of Shore hardness and a slight change in softening and glass transition temperature. A formulation with diethylene glycol yielded a soft PU product with hardness 50-65 Shore A, good elongation and relatively high softening temperature.

3.1. IR Spectroscopy

IR spectra of the polymers were used to confirm the formation of PUs.

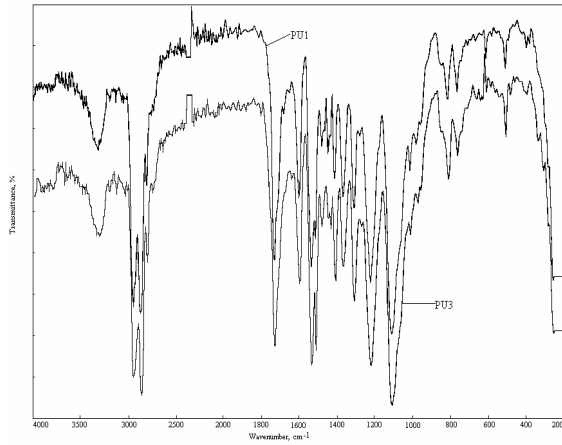


Fig. 1. IR spectra of aromatic polyurethane samples synthesized with EG.

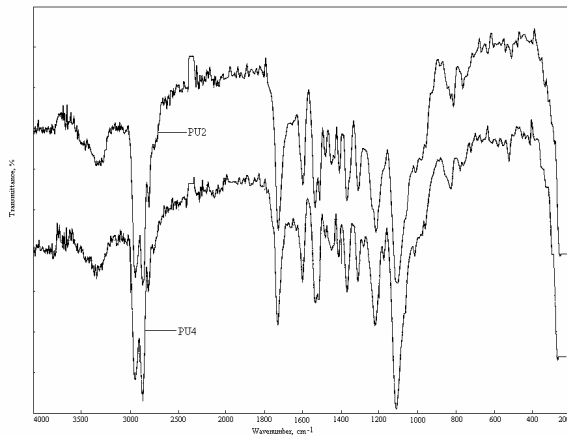


Fig. 2. IR spectra of aromatic polyurethane samples synthesized with DEG.

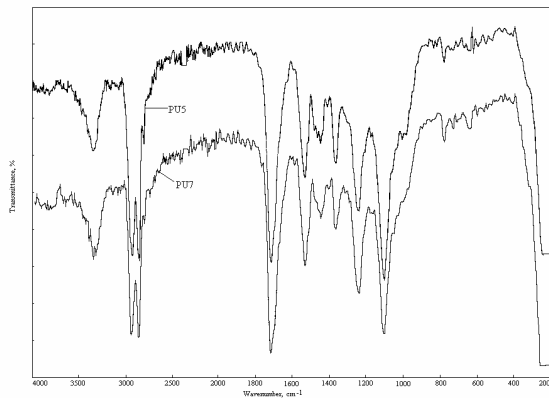


Fig. 3. IR spectra of aliphatic polyurethane samples synthesized with EG.

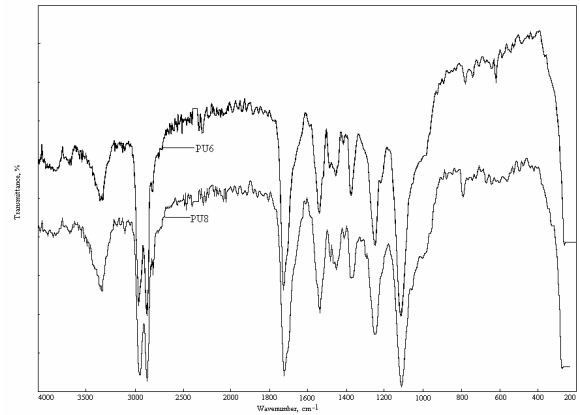


Fig. 4. IR spectra of aliphatic polyurethane samples synthesized with DEG.

Formation of the polymer was confirmed by the disappearance of NCO peak from 2260 cm^{-1} . Appearance of new sharp peak for N-H stretch and for NHCOO (urethane) at 1740 cm^{-1} verifies the formation of polyurethane. The C-O-C stretching frequency (1370 cm^{-1}) for ether with the inclusion of polyether in the polymer chain. Similarly the peak for CH_2 stretch appears to 1470 cm^{-1} . Participation in hydrogen bonding decreases the frequency of the NH vibration and increases its intensity, making this absorption useful in the study of hydrogen-bond effects. The peak is located at about $2980\text{--}2990\text{ cm}^{-1}$ in the spectra (Figs. 1-4), which is characteristic of hydrogen-bonded NH groups.

3.2. Thermogravimetric analysis

Representative thermogravimetric (TG, DTG) curves for various copolymers have been reproduced in Figs. 5-8. However details of degradation temperatures have been elaborated in Tables 3,4.

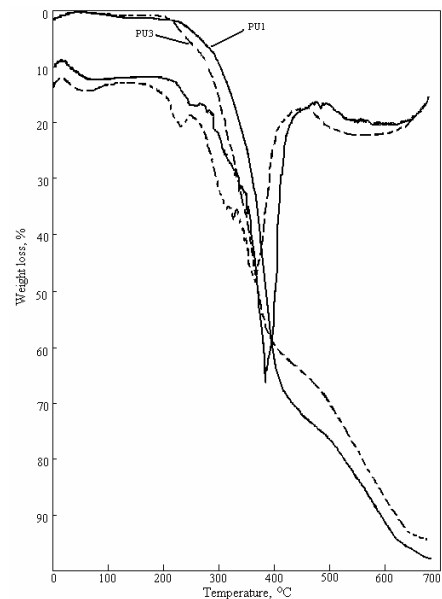


Fig. 5. TG and DTG curves of aromatic polyurethane with EG.

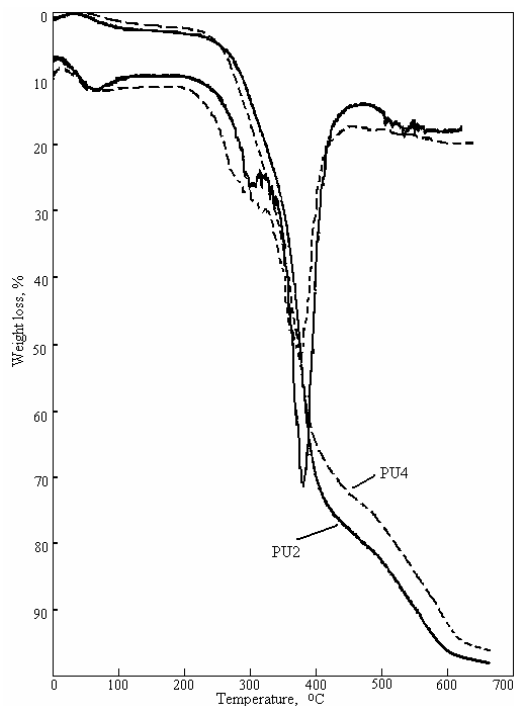


Fig. 6. TG and DTG curves of aromatic polyurethane with DEG.

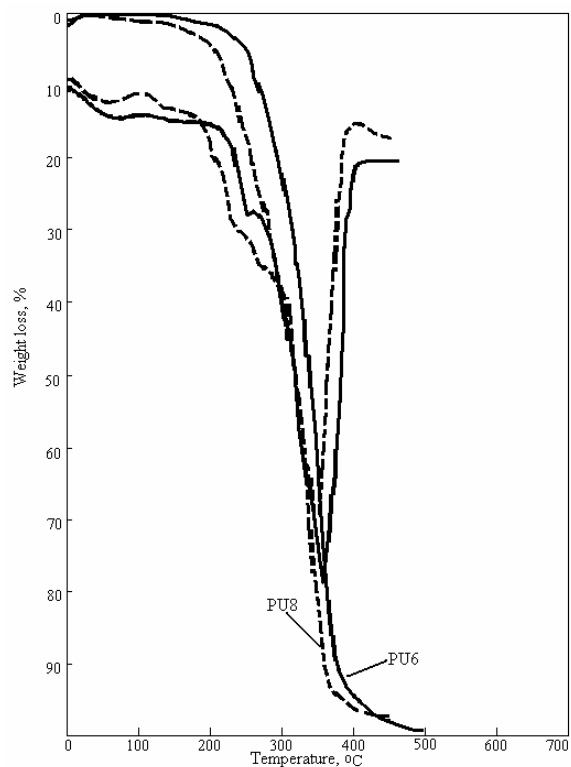


Fig. 8. TG and DTG curves of aliphatic polyurethane with DEG.

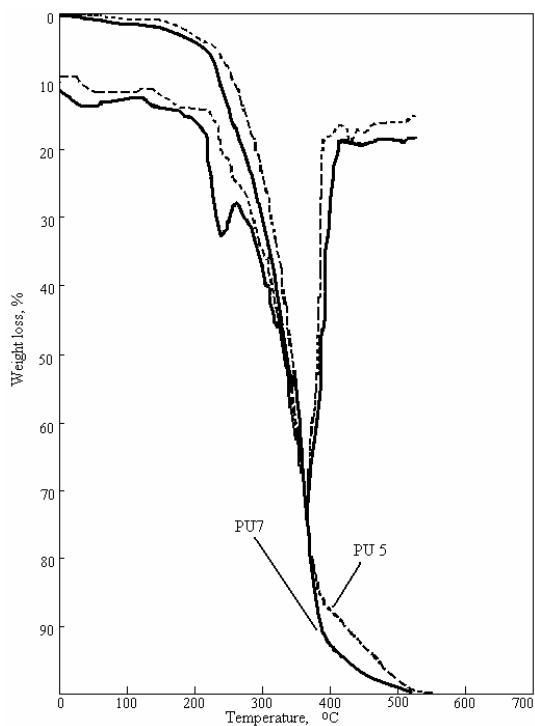


Fig. 7. TG and DTG curves of aliphatic polyurethane with EG.

The open-air TGA was used to study some linear polyether urethanes attempting to outline the increase in the thermal stability brought by components from their structure. The same testing conditions were used for all the copolymer samples being analyzed. The onset (T_i) degradation temperature was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve [15,16].

Table 3. Thermogravimetric data for the aromatic polyurethanes.

Sample code	Weight losses (%) and decomposition temperature ranges			
	Global	Step I	Step II	Step III
PU1	98	10(100-300)	60(300-410)	28(410-700)
PU2	99	9.8 (120-288)	65(288-417)	24,2(417-650)
PU3	94	10.6(115-290)	55(290-470)	28,4(470-660)
PU4	98	9(100-278)	66(278-475)	16(475-680)

Table 4. Thermogravimetric data for the aliphatic polyurethanes.

Sample code	Weight losses (%) and decomposition temperature ranges			
	Global	Step I	Step II	Step III
PU1	99	7(100-240)	77(240-370)	15(370-550)
PU2	99	5 (90-238)	83(238-380)	11(380-490)
PU3	98	6(80-230)	83(230-375)	9(375-520)
PU4	98	7(75-228)	85(228-370)	6(370-470)

The physical crosslinks are important for dimensional stability and to stop cold flow in the uncured materials. The effect of restricting segmental motion in a three dimensional network by chemical crosslink sites is similar of microdomain physical crosslinks except that is irreversible. The crystalline polyether domain acts as an additional physical crosslink site below their melting temperature.

Generally, polyurethanes analyzed decomposed in three steps and the temperature at which the weight losses were maximum is 280-450 °C. The increase of flexible chain lead to relative stability, because the possibility of order the molecular chain is high, following a accentuated decompositions.

Following the initial degradation in the hard segments, the second stage of the degradation was related to the soft segments and started at about 300 °C.

In the DTG curve of polyurethanes, an inflexion is present at about 370 °C for polyurethane with EG and 350 °C for polyurethane with DEG.

The increase in temperature maxim indicates a lower rate in outer diffusion of the degraded products indicated by the lower peak degradation rates exhibited at these temperatures. Thus, it is evident that the cross-linking bridges restrict the diffusion of the degradation products from matrix.

3.3 Mechanical properties

Physico-mechanical analysis evidences the extent of the supermolecular modifications in polyurethanes obtained as a function of their structural modifications. The mechanical properties of polyurethanes with comparable molecular weights were dependent on the hard-segment content.

Stress-strain, modulus and elongation are important for polymer characterization, depending on their structure by varying the polyol and/or diisocyanate molecular weight, as well as variation of chain extenders structure, leading to modifications of stress-strain, modulus and elongation [17]. If the amount of hard segments is greater, higher stress and modulus and lower elongations result. Reverse effects occur with more numerous and longer soft segments.

The shorter soft segment implies that a higher hardness of polyurethane would be obtained. This result may be due to an increase in polar groups and cohesive

energy density. These polar groups, which have a high cohesive force, participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments, resulting in a higher hardness.

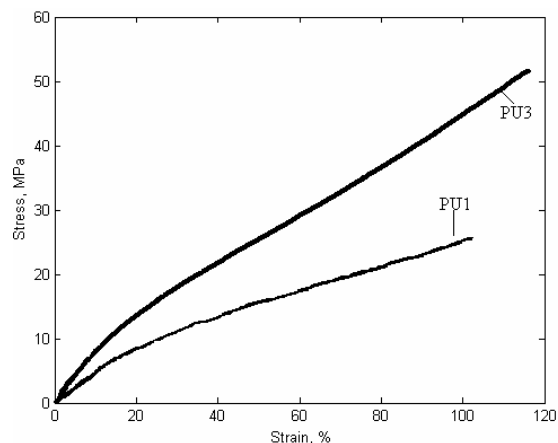


Fig. 9. Stress-strain curves of aromatic polyurethane prepared with EG.

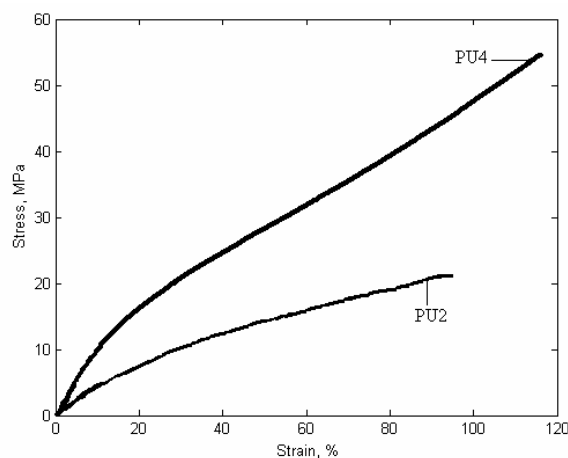


Fig. 10. Stress-strain curves of aromatic polyurethane prepared with DEG.

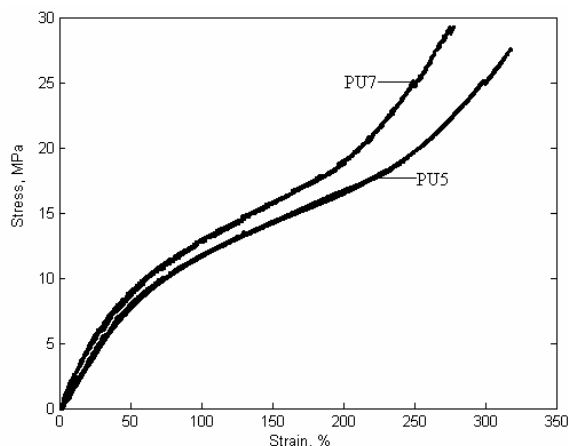


Fig. 11. Stress-strain curves of aliphatic polyurethane prepared with EG.

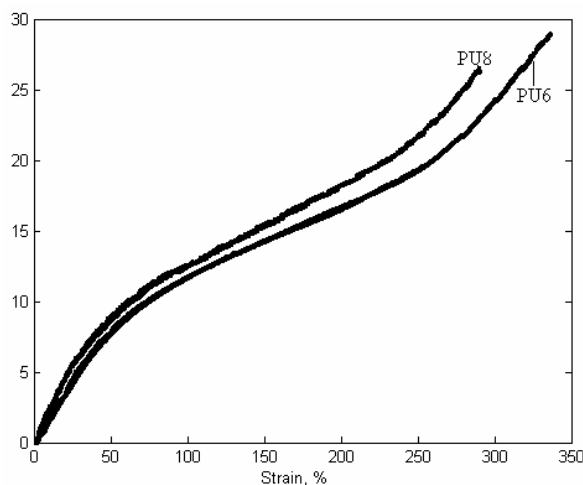


Fig. 12. Stress-strain curves of aliphatic polyurethane prepared with DEG.

The results of physico-mechanical measurements are presented in Table 5, evidencing that an increase of the methylenic group number of the chain extenders employed leads to a lower tensile strength, which may be explained by decreasing concentration of the ether groups on the macromolecular chain.

Table 5. Tensile properties of polyurethanes obtained with aromatic diisocyanates.

Sample code	E ₁ MPa	L1 %	FR MPa	AR %	FM MPa	AM %	E MPa
PU1	11	30.9	23.8	105.37	25	105.3	53
PU2	9.9	36.7	17.2	109.2	19.9	109	25.6
PU3	16.6	26.1	49.1	116.4	51.8	116.4	103
PU4	16.9	20.8	52.6	115.6	54.4	115	155

Table 6. Tensile properties of polyurethanes obtained with aliphatic diisocyanates.

Sample code	E ₁ MPa	L1 %	FR MPa	AR %	FM MPa	AM %	E MPa
PU5	7.2	39.9	24.7	308.8	27.5	308	24.2
PU6	7.8	45	28.9	325.3	28.9	325.2	22.3
PU7	7.6	38.8	29.2	278.2	29.5	278.1	26.4
PU8	7.9	45.1	22.1	287.8	25.8	286	22.7

E₁ – effective modulus to first transformation of phase; L1- elongation to first transformation of phase; FR- tensile stress at break; AR- elongation at break; FM- tensile stress at maximum; AM – elongation at maximum; E- modulus

An ether group develops an intermolecular force of 1.4 Kcal/mole, while a $-CH_2-$ group, only 0.68 Kcal/mole. Effective moduli at 10 % elongation are presented in Table 4; lower moduli for polyurethanes based on DEG, may be observed, compared with the EG based one. The results of physico-mechanical measurements are presented in Table 4, evidencing a

increase of the tensile strength from 17 to 52 MPa, for a rate of reagents 1/2/1 at 1/3/2.

This fact, can be explained by the formation of hydrogen bonds ($NH...O=C<$) with a much higher frequency in the case of 1/3/2 rate, may be explained by the transplanar structure formed [18].

Therefore, for the DEG-based polyurethanes, an increase in the applied stress causes an increase of the forces impeding deformation by the rearrangement of the macromolecules.

Because the crystalline regions play a similar role to crosslinks in improving mechanical properties, the tensile properties of crystallizable material are superior to non-crystallizable material. The influence of molecular weight on the ultimate tensile properties of the hard segment is larger than that of the previously studied factors, especially at low molecular weight. It is clear that, the content of the hard segment increases, and the crosslinking density increase. Varying the chain extenders molecular weight affects the tensile properties of the polyurethanes and the crosslinked materials.

In segment polyurethanes, the mechanical properties were generally accredited to the result of a pseudo-crosslinking effect resulting from the hard-segment aggregation. The hard-segment domain generally exhibits a different order degree or semicrystalline structure, which was considered to be able to reinforce the hard segment domain and, in the case of these polyurethanes, added a crosslinking effect of the glycerine.

Since physical aging would densify and streng then the hard-segment domain from the weakest point, the mechanical properties of the polyurethane may be improved by proper control of the physical aging.

This present study may provide possibilities of enhancing the mechanical property of the polyurethane material.

4. Conclusions

Polyether diols were used for the preparation of elastomeric polyurethanes (PEs) employing prepolymer procedure.

Ethylene and diethylene glycol, glycerine was found to be a suitable chain extender for basical PUs. Depending on the parameters of the formulation, the resulting PUs exhibited hardness about 52-85 Shore A, making them prospective materials falling into the category of the soft grade PUs.

The thermal stability is a function of the components present in the formulation.

Polyurethanes show a three-step thermal degradation. The first stage was associated with the hard segment degradation and the second one, with the soft segments. Higher length of the soft segment and the presence of glycerine linkages increased the polyurethane thermal stability.

Longer chain lengths between crosslinks produce higher elongations at break and lower mechanical moduli. The cross-linking process increases the urethane domain

rigidity and decreases the soft segment crystallinity. These factors enhance the tensile strength of the materials.

Since the amorphous hard segment region is the weakest part of the polyurethane hard phase, densifying the amorphous hard segment region by proper physical raising crosslinking, greatly reinforces the hard phase integrity and thus greatly improves the mechanical properties of the polyurethane materials.

Acknowledgement

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